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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

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TITLE: ANOMALOUS EXPANSION MATERIALS

**AMENDED CLAIMS**

1. (original) A method for controlling the thermal expansion behaviour of a material comprising the step of incorporating into the material a component including one or more diatomic bridges, the or each bridge extending between two atoms in the component, characterised in that the or each diatomic bridge has at least one vibrational mode that causes the two atoms on either side of the bridge to be moved together to a similar or greater extent than competing vibrational mode(s) that cause the two atoms on either side of the bridge to be moved apart.
2. (original) A method as claimed in claim 1 wherein the component comprises a portion or the entirety of the material.
3. (currently amended) A method as claimed in claim 1 or 2 wherein the component comprises a portion of the material in an amount or manner that predetermines the material thermal expansion behaviour.
4. (currently amended) A method as claimed in ~~any one of the preceding claims~~ claim 1 wherein the diatomic bridge has at least two vibrational modes  $\delta 1$  and  $\delta 2$  (as herein defined).
5. (currently amended) A method as claimed in ~~any one of the preceding claims~~ claim 1 wherein the material comprises a plurality of diatomic bridges throughout an infinite molecular coordination network defining a lattice structure, such that changes in lattice geometry induce material negative thermal expansion behaviour.
6. (currently amended) A method as claimed in ~~any one of the preceding claims~~ claim 1 wherein the diatomic bridge is linear.
7. (currently amended) A method as claimed in ~~any one of the preceding claims~~ claim 1 wherein the diatomic bridge is defined by a linear cyanide  $-(CN)-$  bridge.
8. (currently amended) A method as claimed in ~~any one of claims 1 to 4~~ claim 1 wherein the diatomic bridge is defined by a carbon monoxide  $-(CO)-$  bridge, a di-nitrogen  $-(NN)-$  bridge, a nitrogen monoxide  $-(NO)-$  bridge or a carbide  $-(CC)-$  bridge.

9. (currently amended) A method as claimed in ~~any one of the preceding claims~~ claim 1 wherein the component comprises a plurality of diatomic bridges and, for at least some of the diatomic bridges, the two atoms that are linked by the diatomic bridge are metals, semi-metals or non-metals.
10. (original) A method as claimed in claim 9 wherein the two atoms on either side of the bridge are different atoms and thermal expansion is tuned by varying the relative ratios between two or more different atoms on either side of the diatomic bridge.
11. (original) A method as claimed in claim 9 or 10 wherein the diatomic bridge is a cyanide ion coordinated to the metal or semi-metal atoms, and one or both metal or semi-metal atoms in turn coordinates one or more other cyanide ions, which in turn bridge to other atoms.
12. (original) A method as claimed in claim 11 wherein each atom alternatively coordinates other ligands.
13. (original) A method as claimed in claim 12 wherein the other ligands are uni- or multi-dentate, including water, alcohols, diols, thiols, oxalate, nitrate, nitrite, sulfate, phosphate, oxide, sulfide, thiocyanate, non-bridging cyanide, cyanate, nitrogen monoxide, carbon monoxide, dinitrogen.
14. (original) A method as claimed in claim 13 wherein the material is an optionally desolvated salt.
15. (currently amended) A method as claimed in claim 13 ~~or 14~~ wherein the component forms part of an assembly that is neutrally, positively or negatively charged.
16. (original) A method as claimed in claim 15 wherein when the assembly carries a charge, counter-ions are incorporated within cavities within the assembly to provide neutrally charged materials.
17. (original) A method as claimed in claim 16 wherein the counter-ions influence the thermal behaviour of the material, and counteract negative thermal expansion behaviour of the material.
18. (currently amended) A method as claimed in claims 16 ~~or 17~~ wherein the material is porous.
19. (original) A method as claimed in claim 18 wherein the counter-ions are included into pores of the material.
20. (currently amended) A method as claimed in ~~any one of claims 16 to 19~~ claim 16 wherein the counter-ions are varied either by ion exchange or synthetic modification,

to vary the thermal behaviour of the material.

**21.** (currently amended) A method as claimed in ~~any one of claims 13 to 20~~ claim 13 wherein the material comprises guest molecules located in interstitial cavities within a lattice thereof.

**22.** (original) A method as claimed in claim 21 wherein the guest molecules influence the thermal behaviour and optionally counteract negative thermal expansion behaviour of the material.

**23.** (currently amended) A method as claimed in claim 21 ~~or 22~~ wherein the material is porous and the guest molecules are located in pores of the material.

**24.** (currently amended) A method as claimed in ~~any one of claims 21 to 23~~ claim 21 wherein the guest molecules are varied either by sorption/desorption or synthetic modification, to vary the thermal behaviour of the material.

**25.** (currently amended) A method as claimed in ~~any one of claims 21 to 24~~ claim 21 wherein the guest molecules comprise one or more of water, alcohols, organic solvents or gas molecules.

**26.** (currently amended) A method as claimed in ~~any one of claims 13 to 25~~ claim 13 wherein the material has a topology based on a diamond-, wurzite-, quartz-, cubic-, (4,4)-, (6,3)-, (10,3)-, PtS-, NbO-,  $\text{Ge}_3\text{N}_4$ -,  $\text{ThSiO}_2$ - or  $\text{PtO}_x$ -type net.

**27.** (original) A method as claimed in claim 26 wherein the material comprises more than one interpenetrating net of the same or different topology.

**28.** (currently amended) A method as claimed in ~~any one of the preceding claims~~ claim 1 wherein the material comprises zero-dimensional bridged moieties, such as CN bridged molecular squares.

**29.** (original) A method for controlling the thermal expansion behaviour of a material comprising the step of incorporating into the material a component including one or more multi-atomic bridges, the or each bridge extending between two atoms in the material, characterised in that the or each multi-atomic bridge has at least one vibrational mode that causes the two atoms on either side of the bridge to be moved together to a similar or greater extent than competing vibrational mode(s) that cause the two atoms on either side of the bridge to be moved apart.

**30.** (currently amended) A method as claimed in claim 29 wherein the component comprises diatomic bridges as defined in ~~any one of claims 4 to 13~~ claim 4, or polyatomic bridges such as cyanamide, dicyanamide, tricyanomethanide,

thiocyanate, selenocyanate, cyanate, isothiocyanate, isoselenocyanate, isocyanate, azide, cyanogen or butadiynide.

31. (cancelled)

32. (cancelled)

33. (cancelled)

34. (cancelled)

35. (original) A method for altering the thermal expansion behaviour of a material that comprises a component having a plurality of diatomic bridges, each bridge extending between two atoms in the component and having at least one vibrational mode that causes the two atoms on either side of the bridge to be moved together to a similar or greater extent than competing vibrational mode(s) that cause the two atoms on either side of the bridge to be moved apart, the method comprising the step of incorporating into the component two or more different atoms such that, for at least some of the diatomic bridges, the two atoms on either side of the bridge are different.

36. (original) A method as claimed in claim 35 wherein the thermal expansion is tunable by varying the relative ratios between the two or more different atoms on either side of the diatomic bridge.

37. (original) A method as claimed in claim 35 or 36 wherein the two atoms on either side of the bridge are different metals, semi-metals or non-metals, or combinations thereof.

38. (cancelled)

39. (currently amended) A material having a thermal expansion behaviour controlled by the method of ~~any one of the preceding claims~~ claim 1.

40. (original) A material as claimed in claim 39 comprising one or more of:

(a) materials based on the  $\text{Zn}(\text{CN})_2$ -type or  $2 \times (6,4)$  cubic structure (doubly interpenetrating diamond nets), optionally including substitution of divalent metals for some or all of the Zn atoms, including Cd(II), Hg(II), Mn(II), Be(II), Mg(II), Pb(II) and Co(II), and optionally comprising substitution of mixtures of univalent, and optionally divalent and trivalent metal ions for Zn to give materials of the form:

$$\{(\text{M1}_1^{\text{II}})_{x1}(\text{M1}_2^{\text{II}})_{x2} \dots (\text{M1}_n^{\text{II}})_{xn}\} \{(\text{M2}_1^{\text{I}})(\text{M3}_1^{\text{III}})\} y1 \{(\text{M2}_2^{\text{I}})(\text{M3}_2^{\text{III}})\} y2 \dots$$

$$\{(\text{M2}_m^{\text{I}})(\text{M3}_m^{\text{III}})\} ym (\text{CN})_2$$
 where  $\text{M1}_i$  includes Zn(II), Cd(II), Hg(II), Mn(II), Be(II),

Mg(II), Pb(II) and Co(II);  $\text{M2}_j$  includes Li(I) and Cu(I);  $\text{M3}_k$  includes Al(III), Ga(III) and

In(III); n and m being any non-negative whole numbers with at least one greater than

or equal to unity; and  $(x_1 + x_2 + \dots + x_n) + 2 \times (y_1 + y_2 + \dots + y_m) = 1$ ; and  $i, j$  and  $k$  being any positive integer;

(b) materials of (a) but with a single diamond-type network rather than two interpenetrating networks, optionally with other ions or molecules incorporated into the structure, optionally with the inclusion of lower- or higher-valent metals into the network lattice;

(c) materials of (a) and (b) but with more than two interpenetrating diamond networks;

(d) materials based on  $\text{Ga}(\text{CN})_3$ -type structure, optionally satisfying the general formula:

$\{(M1_1^{\text{III}})_{x_1}(M1_2^{\text{III}})_{x_2} \dots (M1_n^{\text{III}})_{x_n}\} \{(M2_1^{\text{II}})(M3_1^{\text{IV}})\}_{y_1} \{(M2_2^{\text{II}})(M3_2^{\text{IV}})\}_{y_2} \dots \{(M2_m^{\text{II}})(M3_m^{\text{IV}})\}_{y_m} (\text{CN})_3$  where  $M1$  includes trivalent metal ions including  $\text{Fe}(\text{III})$ ,  $\text{Co}(\text{III})$ ,  $\text{Cr}(\text{III})$ ,  $\text{Ti}(\text{III})$ ,  $\text{Al}(\text{III})$ ,  $\text{Ir}(\text{III})$ ,  $\text{Ga}(\text{III})$ ,  $\text{In}(\text{III})$  and  $\text{Sc}(\text{III})$ ;  $M2$  includes divalent metal ions including  $\text{Mg}(\text{II})$ ,  $\text{Zn}(\text{II})$ ,  $\text{Cd}(\text{II})$ ,  $\text{Co}(\text{II})$ ,  $\text{Fe}(\text{II})$ ,  $\text{Ru}(\text{II})$ ,  $\text{Mn}(\text{II})$  and  $\text{Ni}(\text{II})$ ;  $M3$  includes tetravalent metal ions such as  $\text{Pd}(\text{IV})$  and  $\text{Pt}(\text{IV})$ ;  $n$  and  $m$  being non-negative whole numbers with at least one greater than or equal to unity; and  $(x_1 + x_2 + \dots + x_n) + 2 \times (y_1 + y_2 + \dots + y_m) = 1$ ;

(e) materials of (d) but with other ions or molecules being incorporated in the structure, including lower- or higher-valent metals in the network lattice;

(f) materials of (d) to (e) but with more than one interpenetrating cubic framework;

(g) other simple metal cyanides not explicitly belonging to (a) to (f) of the general form:  $(M1^{n_1+})_{x_1}(M2^{n_2+})_{x_2} \dots (Mk^{n_k+})_{x_k} (\text{CN})_i \cdot \{\text{guest}\}$  where  $M1, M2 \dots Mk$  were metals with oxidation states  $n_1+, n_2+ \dots n_k+$  respectively;  $k$  and  $i$  were positive whole numbers;  $(x_1 \times n_1) + (x_2 \times n_2) + \dots + (x_k \times n_k) = i$ ; and  $\{\text{guest}\}$ , when present, includes any solvent or molecular species such as water, alcohols, organic solvents or gas molecules, optionally including single or multiple interpenetrating regular nets including quartz,  $\text{NbO}$ ,  $\text{PtS}$ ,  $\text{Ge}_3\text{N}_4$ ,  $(10,3)$ ,  $\text{ThSiO}_2$ ,  $\text{PtO}_x$  or wurtzite nets;

(h) materials of (g) but with other ions or molecules incorporated into the structure, including lower- or higher-valent metals in the network lattice;

(i) materials other than (h) comprising more than one type of network lattice;

(j) materials as in (a) to (i) but with metal and/or cyanide vacancies within the structure;

(k) materials other than (a) to (j) comprising cyanide-bridged atoms, including cyanide-bridged materials in which the coordination spheres of some or all metal

atoms include one or more non-cyanide bridges, including water, alcohols, diols, thiols, oxalate, nitrate, nitrite, sulfate, phosphate, oxide, sulfide, thiocyanate, (non-bridging) cyanide, cyanate, nitrogen monoxide, carbon monoxide or dinitrogen, optionally comprising regular nets, and optionally including interstitial ions or guest molecules;

(l) materials of (k) that comprise finite cyanide-bridged moieties, optionally comprising cyanide-bridged polyhedra, polygons or finite chains, optionally comprising branches and components unrelated or unconnected to the cyanide-bridged moieties;

(m) materials of (a) to (l) where chemical composition is varied within the one crystal/crystallite by variation of crystallisation conditions, including concentrations and temperatures during crystallisation;

(n) materials of (a) to (l) where structure type, guest inclusion or ion inclusion is varied within the one crystal/crystallite; and

(o) amorphous materials or glasses based on any one of (a) to (n).

**41.** (original) A material as claimed in claim 40 wherein:

\* material (a) comprises  $\text{Zn}(\text{CN})_2$ ,  $\text{Zn}_{0.8}\text{Cd}_{0.2}(\text{CN})_2$ ,  $\text{Zn}_{0.64}\text{Cd}_{0.36}(\text{CN})_2$ ,  $\text{Cd}(\text{CN})_2$ ,  $\text{Mn}(\text{CN})_2$ ,  $\text{Zn}_{0.5}\text{Hg}_{0.5}(\text{CN})_2$ ,  $\text{Li}_{0.5}\text{Ga}_{0.5}(\text{CN})_2$  and  $\text{Cu}_{0.5}\text{Al}_{0.5}(\text{CN})_2$ ;

\* material (b) comprises  $\text{Cd}(\text{CN})_2 \cdot \frac{1}{2}\text{CCl}_4$ ,  $[\text{NMe}_4]_{0.5}[\text{Cu}^{\text{I}}_{0.5}\text{Zn}^{\text{II}}_{0.5}(\text{CN})_2]$ ,  $\text{Cd}(\text{CN})_2 \cdot \text{CMe}_4$ ,  $\text{Cd}(\text{CN})_2 \cdot \text{CMe}_3\text{Cl}$ ,  $\text{Cd}(\text{CN})_2 \cdot \text{CMe}_2\text{Cl}_2$ ,  $\text{Cd}(\text{CN})_2 \cdot \text{CMeCl}_3$ ,  $\text{Cd}(\text{CN})_2 \cdot \text{CCl}_4$ ,  $\text{Cd}_{0.5}\text{Hg}_{0.5}(\text{CN})_2 \cdot \text{CCl}_4$ ,  $\text{Cd}_{0.5}\text{Zn}_{0.5}(\text{CN})_2 \cdot \text{CCl}_4$ ;

\* material (d) comprises  $\text{Ga}^{\text{III}}(\text{CN})_3$ ,  $\text{Co}^{\text{III}}(\text{CN})_3$ ,  $\text{Al}^{\text{III}}(\text{CN})_3$ ,  $\text{Cd}^{\text{II}}_{0.5}\text{Pt}^{\text{IV}}_{0.5}(\text{CN})_3$  and  $\text{Zn}^{\text{II}}_{0.5}\text{Pt}^{\text{IV}}_{0.5}(\text{CN})_3$ ;

\* material (e) comprises the Prussian blues compounds such as  $\text{K}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CN})_6]$ , and their analogues such as  $\text{Cs}_2[\text{Li}^{\text{I}}\text{Fe}^{\text{III}}(\text{CN})_6]$ ,  $\text{Cd}^{\text{II}}_{0.5}\text{Pt}^{\text{IV}}_{0.5}(\text{CN})_3 \cdot \text{H}_2\text{O}$ ,  $\text{Zn}^{\text{II}}_{0.5}\text{Pt}^{\text{IV}}_{0.5}(\text{CN})_3 \cdot \text{H}_2\text{O}$ ,  $\text{K}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}(\text{CN})_6] \cdot x\text{H}_2\text{O}$ ;

\* material (g) comprises  $\text{Ag}^{\text{I}}\text{CN}$ ,  $\text{Au}^{\text{I}}\text{CN}$ ,  $\text{Zn}^{\text{II}}\text{Ag}^{\text{I}}_2(\text{CN})_4$ ,  $\text{Zn}^{\text{II}}\text{Au}^{\text{I}}_2(\text{CN})_4$ ;

\* material (h) comprises  $\text{KCd}^{\text{II}}[\text{Ag}^{\text{I}}(\text{CN})_2]_3$  and  $\text{KCd}^{\text{II}}[\text{Au}^{\text{I}}(\text{CN})_2]_3$ ;

\* material (i) comprises  $\text{Zn}^{\text{II}}\text{Ag}^{\text{I}}_2(\text{CN})_4 \cdot 0.575\text{Ag}^{\text{I}}\text{CN}$ ;

\* material (j) comprises  $\text{Mn}^{\text{II}}\text{Co}^{\text{III}}_{0.33}\text{Cr}^{\text{III}}_{0.33}(\text{CN})_4$ ,  $\text{Cd}^{\text{II}}\text{Fe}^{\text{III}}_{0.33}\text{Co}^{\text{III}}_{0.33}(\text{CN})_4$ ,  $\text{Cd}^{\text{II}}\text{Co}^{\text{II}}_{0.33}\text{Ir}^{\text{II}}_{0.33}(\text{CN})_4$ ,  $\text{Pd}^{\text{II}}\text{Cr}^{\text{II}}_{0.33}\text{Ir}^{\text{II}}_{0.33}(\text{CN})_4$  and  $\text{Cu}^{\text{II}}\text{Co}^{\text{III}}_{0.66}(\text{CN})_4$ ;

\* material (k) comprises  $\text{Ni}^{\text{II}}(\text{CN})_2 \cdot x\text{H}_2\text{O}$ ,  $\text{Fe}_4[\text{Re}_6\text{Se}_8(\text{CN})_6]_3 \cdot 36\text{H}_2\text{O}$ ,  $\text{Cd}^{\text{II}}\text{Ni}^{\text{II}}(\text{CN})_4 \cdot x\text{H}_2\text{O}$  and  $\text{Cd}^{\text{II}}\text{Pt}^{\text{II}}(\text{CN})_4 \cdot x\text{H}_2\text{O}$ ; and

\* material (m) comprises  $\text{Zn}_x\text{Cd}_{1-x}(\text{CN})_2$ .

**42.** (original) A material that comprises a component having a plurality of diatomic bridges, each bridge extending between two atoms in the component and having at least one vibrational mode that causes the two atoms on either side of the bridge to be moved together to a similar or greater extent than competing vibrational mode(s) that cause the two atoms on either side of the bridge to be moved apart, wherein, for at least some of the diatomic bridges, the two atoms on either side of the bridge are different.

**43.** (original) A material as claimed in claim 42 wherein the two atoms on either side of the bridge are different metals, semi-metals or non-metals, or combinations thereof.

**44.** (currently amended) A composite incorporating a material as claimed in ~~any one of claims 40 to 43 or incorporating a material produced by the method of any one of claims 1 to 38~~ claim 40 or 41.

**45.** (currently amended) A composite as claimed in claim 44 comprising two or more different materials, at least one of which is produced by the method of ~~any one of the claims 1 to 38~~ claim 1 or 29.

**46.** (original) A composite as claimed in claim 45 further comprising a binding agent for the two or more different materials.

**47.** (currently amended) A composite as claimed in claim 45 including a material produced by the method of ~~any one of the claims 1 to 38~~ claim 1 or 29 together with an unrelated material (as herein defined).

**48.** (original) A composite as claimed in claim 47 further comprising a binding agent for the material and unrelated material.

**49.** (currently amended) A device formed from or comprising material having controllable thermal expansion behaviour, the material being produced by a method as claimed in ~~any one of claims 1 to 38~~ claim 1, or being as claimed in ~~any one of claims 40 to 48~~ claim 40 or 41.

**50.** (original) A device as claimed in claim 49 that is: an optical fibre; a laser; an optical, electronics or thermal electronics component; a substrate or support for an optical component, electronics device or thermal electronics device; a thermal transfer device; a zero insertion force socket; a component for a superconductor, high precision instrument or frequency resonator; an optical device displaying birefringence or that is optically transparent; an interference device;

or a device that displays: piezoelectric properties; optical activity; or nonlinear optical properties.

**51.** (original) A method for directing the thermal expansion behaviour of a material comprising the step of incorporating into the material a component including one or more diatomic bridges, the or each bridge extending between two atoms in the component, with the or each diatomic bridge having at least one vibrational mode that causes the two atoms on either side of the bridge to be moved together to a similar or greater extent than competing vibrational mode(s) that cause the two atoms on either side of the bridge to be moved apart, characterised in that the component comprises an anisotropic single crystal that, by virtue of its alignment in the material, directs thermal expansion.

**52.** (original) A material having directed thermal expansion behaviour, the material being produced by the method of claim 51.

**53.** (currently amended) A method as claimed in claim 51 ~~or a material as claimed in claim 52~~ wherein the component comprises a portion or the entirety of the material.

**54.** (new) A material as claimed in claim 52 wherein the component comprises a portion or the entirety of the material.